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COMPLETE SPECIFICATION

Compositions containing Glycidyl Polyethers of Dihydric Phenols

We, NAAMLooZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carcl van Bylandtlaan, The Hague, The Netherlands, a company organised under the laws of The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new compositions of matter containing glycidyl polyethers of dihydric phenols, which compositions cure to hard tough resinous materials upon addition thereto of a curing agent and are particularly but not exclusively suitable for adhesive, potting, casting and surface coating purposes.

Useful resins have been prepared heretofore by curing a glycidyl polyether of a dihydric phenol with the aid of various curing agents such as amines, dicarboxylic acid anhydrides, and certain acids. The resin-forming ingredient employed for this purpose is the glycidyl polyether of a dihydric phenol. The glycidyl

polyether is obtainable by reacting at about 50° C. to 150° C. at least one mol of epichlorhydrin with one mol of dihydric phenol in the presence of a base such as sodium or potassium hydroxide in amount of about 2 to 30% stoichiometric excess of base to the dihydric phenol. Glycidyl polyethers of low molecular weight are obtainable by mixing a large excess such as about 4 to 10 mols of epichlorhydrin with one mol of dihydric phenol and adding an alkali to the heated mixture while the reaction progresses, the addition of the alkali being regulated so that the reaction mixture is kept at or near the neutral point. The unreacted excess of epichlorhydrin is removed by distillation from the resulting reaction product. The polyethers are also obtainable by substituting 1,3-dichloro-isopropanol for the epichlorhydrin in the noted methods and using about twice the amount of base.

The predominant constituent of the glycidyl polyether of dihydric phenol is represented by the formula.



wherein R represents the divalent aromatic hydrocarbon radical (which was linked directly to the two hydroxyl groups of starting dihydric phenol), and n is any integer. The glycidyl polyether also contains a small proportion of compounds of similar structure wherein one or both of the glycidyl radicals are replaced by 2,3-dihydroxypropyl radicals (from hydration of glycidyl radicals) and/or 3-chloro-2-hydroxypropyl radicals (from incomplete dehydrochlorination). The glycidyl polyether is thus seen to have a chain of alternating glyceryl and divalent radicals united through ether oxygen with glyceryl radicals in terminal position. The ether oxygen (as distinguished from epoxy oxygen and hydroxyl oxygen is linked to the primary carbon atoms of the glyceryl radicals. The excess valencies of the glyceryl radicals over those which link epoxide and ether oxygen link and chemically bind hydroxyl groups and chlorine atoms of the hydrated and hyd-

rochlorinated glycidyl groups in the molecule.

The molecular weight of the glycidyl polyether, which is reflected in the value of n in the above formula, is dependent upon the ratio of epichlorhydrin (or the substitute therefor) to dihydric phenol employed in preparing the polyether. The use of a ratio of about 1.25 mols of epichlorhydrin per mol of dihydric phenol gives glycidyl polyether of intermediate molecular weight and chain length. By increasing the ratio of epichlorhydrin to dihydric phenol, the molecular weight is decreased. If the mole ratio of epichlorhydrin to dihydric phenol is about 10:1 the product is essentially the diglycidyl diether of the dihydric phenol with n equal to or closely approaching zero. Likewise, the use of decreasing ratios of epichlorhydrin to dihydric phenol down to a ratio of 1:1 gives products of higher molecular weight.

Although a glycidyl polyether of the highest molecular weight is obtainable by use of low

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ratios of epichlorohydrin to dihydric phenol, it is preferred to effect preparation by a different method owing to the fact that removal of the formed salt and excess base from the higher products is so difficult. By reacting less than an equivalent amount of dihydric phenol with a previously prepared glycidyl polyether of dihydric phenol of intermediate molecular weight, there is obtained glycidyl polyether of high molecular weight. The reaction is effected by heating and mixing the dihydric phenol with the intermediate molecular weight glycidyl polyether in a melt and maintaining the temperature at about 150° C. to 200° C. for several hours' time whereby the thermoplastic glycidyl polyether of high molecular weight is obtained.

In using the glycidyl polyether of a dihydric phenol in many applications such as for adhesive, potting, casting and like purposes, it is desirable and customary to employ a polyether which is a mobile liquid at ordinary temperature so as to facilitate spreading or pouring thereof, and such glycidyl polyethers are found amongst those having a low molecular weight. The glycidyl polyether is usually employed in the applications just mentioned in undiluted conditions because incorporation of most inert viscosity reducing solvents with the polyether gives a cured resin which has greatly reduced physical strength as compared to the cured resin from undiluted polyether. While considerable success has been obtained in using a normally liquid glycidyl polyether of a dihydric phenol in adhesive and potting applications, the resulting cured resin lacks certain desirable properties. The cured resin is unduly brittle and lacks desired toughness.

We have now found that a cured resin of improved properties, particularly improved adhesive properties, can be obtained from a mixture of two different glycidyl polyethers of a dihydric phenol wherein a small proportion of glycidyl polyether of high molecular weight is in admixture with glycidyl polyether of low molecular weight.

According to the present invention there is provided a composition of matter comprising a first glycidyl polyether of a dihydric phenol in admixture with an added 3% to 20% by weight of a second glycidyl polyether of a dihydric phenol, said first glycidyl polyether having a Durrans' Mercury Method melting point below 30° C., a 1,2-epoxy equivalency as hereinafter defined between 1.6 and 2.0 and containing 1 to 1.5 of the aromatic radicals in the average molecule thereof; and said second glycidyl polyether having a Durrans' Mercury Method melting point above 75° C., a 1,2-epoxy equivalency as hereinafter defined of 1.2 to 1.8 and containing at least 4 of the aromatic radicals in the average molecule thereof. The said composition is thus glycidyl polyether of a dihydric phenol of short chain length having low melting point so as to be liquid at

normal temperature in admixture with a small proportion of glycidyl polyether of a dihydric phenol of long chain length having a high melting point so as to be a solid at normal temperature. The dihydric phenol from which the two glycidyl polyethers are derived can be the same or different.

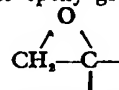
The Durrans' Mercury Method melting point of the polyethers means the melting point as determined by the method of T. H. Durrans '76 for thermoplastic materials described in J. Oil and Colour Chem. Assoc., 12, 173-5 (1929). The method gives quite accurate and reproducible results.

The number of aromatic radicals in the average molecule of the glycidyl polyether of a dihydric phenol is equal to $n + 1$ wherein n is as described above with respect of the structural formula of the glycidyl polyethers. The value of n is related to the molecular weight of the glycidyl polyethers. The molecular weight is conveniently measured by the customary ebullioscopic method with use of ethylene dichloride as solvent for the glycidyl polyether. The value of n is calculated from the formula

$$n = \frac{M - A - 146}{A + 90}$$

wherein M is the measured molecular weight of the glycidyl polyether, and A is the molecular weight of the divalent aromatic radical contained in the polyether, i.e. the calculated molecular weight of the aromatic radical which is linked directly to the two hydroxyl groups of the dihydric phenol from which the glycidyl polyether is derived.

The 1,2-epoxy equivalency of the glycidyl polyether is defined for the purpose of the present specification and the appended claims as the number of epoxy groups.



contained in the average molecule of the glycidyl polyether. The 1,2 epoxy equivalency is equal to the measured molecular weight divided by the epoxide equivalent weight. The epoxide equivalent weight is the weight of glycidyl polyether which contains and is equivalent to one 1,2-epoxy group. It is determined by heating a weighed sample of the polyether with an excess of 0.2N pyridinium chloride in chloroform solution at the boiling point under reflux for two hours whereby the pyridinium chloride quantitatively hydrochlorinates the epoxy groups to chlorhydrin groups. After cooling, the excess pyridinium chloride is back-titrated with 0.1N sodium hydroxide in methanol to the phenol-phthalein end point. The epoxide equivalent weight is calculated by considering that each molecule of consumed HCl from the pyridinium chloride combines with an epoxy group.

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The composition of the present invention are prepared by mixing the proper proportion of high melting glycidyl polyether with the low melting polyether. In order that the desired homogeneous mixture will be obtained, it is convenient to add the high melting polyether in finely divided or powdered condition to the low melting polyether which is heated to about 50° C. to 125° C. The mixture is then maintained hot, and is stirred until the mixture homogenizes with solution of the solid polyether in the melt. If desired, the high melting constituent may also be melted before addition to the low melting component.

The low melting component of the compositions is glycidyl polyether derived from any one of various dihydric phenols. Suitable dihydric phenols include and are exemplified by, but not limited to, such compounds, as resorcinol, 1,1-bis(4-hydroxyphenyl) ethane, 1,1-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)-2-methylpropane, 3-3-bis(4-hydroxyphenyl)pentane, and 1,1-bis(4-hydroxyphenyl)-2-ethylhexane. Also suitable are isomeric compounds to those listed above wherein the phenolic hydroxyl groups are in the 2,4' positions and the 2,2' positions. The dihydric phenols are seen to be free from functional groups other than the phenolic hydroxyl groups.

Although the compositions may contain a glycidyl polyether of a dihydric phenol which has a Durrans' melting point between 20° C. and 30° C. as major component, the desirable properties are best obtained with compositions containing a polyether having a melting point below about 15° C. Preferably the low melting constituent is glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane having a melting point below 15° C. Particularly from about 5° C. to 12° C. Another very suitable low melting component is the glycidyl polyether of 1,1-bis(4-hydroxyphenyl)ethane.

As explained before, the dihydric phenol from which the low melting and high melting glycidyl polyether is derived can be either the same or different. It is generally preferred that both glycidyl polyethers be derived from a single dihydric phenol, and that it be 2,2-bis(4-hydroxyphenyl)propane. However, excellent results are obtained with compositions containing a low melting glycidyl polyether of 1,1-bis(4-hydroxyphenyl)ethane and a high melting glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane.

The high melting component of the compositions is glycidyl polyether of a dihydric phenol that has a Durrans' melting point above 75° C. and contains at least four ($n+1$) of the aromatic radicals from the dihydric phenol. The aromatic radical is the whole divalent hydrocarbon radical of the dihydric phenol, i.e. the radical which was linked directly to

the two phenolic hydroxyl groups of the dihydric phenol. For example, the aromatic radical contained in glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane is the 2,2-bis(4-phenylene) propane radical, and that in the polyether of 1,1-bis(4-hydroxyphenyl)ethane is the 1,1-bis(4-phenylene)ethane radical.

While the long chain constituent of the composition has a Durrans' melting point above 75° C. best results are obtained with a glycidyl polyether having a melting point considerably above this minimum. Excellent results are obtained with a polyether having a melting point of at least 125° C. There appears to be no particular upper limit to the melting point for suitability, but generally it is not greater than about 180° C. The glycidyl polyethers having a melting point between 125° C. and 180° C. which contain 6 to 15 of the aromatic radicals in the average molecule thereof are very suitable. Particularly preferred high melting glycidyl polyether for use in the compositions is the glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane having a melting point of from 140° C. to 160° C. All of the high melting glycidyl polyethers having a 1,2-epoxy equivalency of about 1.2 to 1.8.

The high melting glycidyl polyethers can be derived from any or the particular dihydric phenols described above in connection with the low melting polyethers. If desired, the high melting polyethers can be prepared from other dihydric phenols such as, for example, 4,4'-dihydroxy-diphenyl, bis(4-hydroxyphenyl) methane, 2,2-bis(4-hydroxy-2-methylphenyl) propane, 2,2-bis(4-hydroxy-2-tertiarybutylphenyl) propane, bis(2-hydroxynaphthyl)methane and 1,5-dihydroxynaphthalene. These dihydric phenols are also free from functional groups other than the two phenolic hydroxyl groups.

The compositions of the present invention consist essentially of the low melting glycidyl polyether in admixture with about an added 3% to 20% by weight of the high melting glycidyl polyether, i.e. the compositions contain 100 parts by weight of low melting constituent and about 3 to 20 parts of high melting component. Very suitable compositions contain about an added 5% to 15% by weight of high melting glycidyl polyether. The compositions may also contain very minor amounts of impurities of various types normally associated with the glycidyl polyethers including free phenolic compounds such as phenol and/or the dihydric phenol from which the polyethers are derived. The compositions may be entirely free from phenols, but in any event, they contain less than about 0.004 equivalent of phenolic hydroxyl per 100 grams.

According to a preferred embodiment of the present invention the composition, comprising a glycidyl polyether of low molecular weight in admixture with a glycidyl polyether of high molecular weight, may also contain 5% to 25%

by weight of a liquid aliphatic polycycloepoxide. Thus the preferred compositions of the invention contain essentially 100 parts by weight of the low melting constituent, about 3 to 20 parts of the high melting component and about 5 to 25 parts of the aliphatic polycycloepoxide.

The aliphatic polycycloepoxides employed as the third component in the preferred composition of the present invention is a mobile liquid having a viscosity of less than about 500 centipoises at 25° C. In being a polycycloepoxide, the substance contains two or more epoxide groups in the molecule. These may be 1,2-epoxide groups in the terminal positions, or they may be non-terminal epoxide groups. In all cases, the two bonds of the epoxide oxygen atom are linked to different saturated carbon atoms which are adjacent and linked directly together. The polycycloepoxide is of aliphatic character and thus free of cyclic aromatic hydrocarbon groups as well as being free from reactive functional groups other than epoxy and hydroxyl groups.

A variety of particular polycycloepoxide compounds and substances are suitable for use in compositions of the present invention. The simplest diepoxide contains at least four carbon atoms as is the case with butadiene dioxide, or 1,2-epoxy-3,4-epoxy-butane. The epoxy groups may be separated from each other by ether, oxygen or sulphur as in bis(2,3-epoxypropyl) ether, bis(2,3-epoxybutyl) ether, bis(2,3-epoxypropyl) thioether and 1,2-bis(2,3-epoxypropoxy)ethane. Also suitable are mobile liquid complex polycycloepoxides obtained from the reaction of at least two mole of epichlorhydrin with a mol of polyhydric alcohol such as glycerol, erythritol, diethylene glycol, pentaerythritol or polyallyl alcohol, in the presence of a catalyst such as BF₃-ether complex followed by dehydrochlorination of the resulting chlorhydrin polyether with a base such as sodium silicate. Epoxidised triglycerides constitute a preferred class of aliphatic polycycloepoxides. These are prepared by epoxidising the olefinic unsaturation contained in the acyl groups of natural oils with per fatty acids such as peracetic or performic acid. For example, see the methods described in United States Patent No. 2,485,160, according to which an unsaturated compound is epoxidized with a mixture of hydrogen peroxide and formic acid at a temperature of 10° to 100° C. said hydrogen peroxide being present in a ratio of 1 to 2 mole, and said formic acid in a ratio of 0.25 to 1.0 mole, for each double bond in each mole of the ester to be epoxidised. Polycycloepoxides of this type include epoxidised soybean, cottonseed peanut, olive, corn, tobacco seed, perilla, castor, linseed, sunflower and safflower oil. These epoxidised vegetable oils are mobile liquids that contain about 2.5 to 5 epoxy groups per molecule. It has been found that epoxidised soybean oil is a particularly suitable member of the preferred class.

The presence of the aliphatic polycycloepoxide in the composition of the present invention adds greatly to its utility. Furthermore, the function of the polycycloepoxide in the composition is unexpected. The mixture of low melting glycidyl polyether of a dihydric phenol containing the small proportion of added high melting glycidyl polyether may be a liquid of such high viscosity that it cannot be conveniently spread at normal temperature in applications as an adhesive. By incorporating the liquid polycycloepoxide therewith, a spreadable composition is obtained. Furthermore, the cured composition retains its high strength properties in spite of the inclusion therein of the liquid aliphatic polycycloepoxide.

The preferred composition of the present invention is prepared by bringing the three components together into a homogeneous mixture. It is convenient to add the high melting glycidyl polyether in finely divided or powdered condition to the low melting polyether which is heated to about 60° C. to 120° C. and to stir the mixture at the elevated temperature until the high melting polyether dissolves. The aliphatic polycycloepoxide is then stirred in to complete the preparation.

The preparation and properties of several typical glycidyl polyethers of dihydric phenols used in compositions of the invention are described below. The parts and percentages are by weight. The first five preparations relate to low melting polyethers.

POLYETHER I.—1

A solution is prepared by dissolving 2,2-bis(4-hydroxyphenyl)propane in slightly aqueous epichlorhydrin in the proportion of 5130 parts (22.5 mols) of the dihydric phenol in 20812 parts (225 mols) of epichlorhydrin and 104 parts of water. The solution is prepared in a kettle provided with heating and cooling equipment, agitator, distillation condenser and receiver. A total of 1880 parts of solid 97.5% sodium hydroxide, corresponding to 2.04 mols of sodium hydroxide per mol of bis-phenol (2% excess) is added in instalments. The first instalment of 300 parts of sodium hydroxide is added and the mixture heated with efficient agitation. The heating is discontinued as the temperature reaches 80° C. and cooling is started in order to remove exothermic heat of reaction. The control is such that the temperature rises only to about 100° C. When the exothermic reaction has ceased and the temperature has fallen to 97° C. a further addition of 316 parts of sodium hydroxide is made and similar further additions are effected at successive intervals. An exothermic reaction takes place after each addition. Sufficient cooling is applied so there is gentle distillation of epichlorhydrin and water, but the temperature is not allowed to go below about 95° C. No cooling is necessary after the final addition of sodium hydroxide. After the last addition of

sodium hydroxide with completion of the reaction, the excess epichlorhydrin is removed by vacuum distillation with use of a kettle temperature up to 150° C. and a pressure of 50 millimetres pressure (mercury). After completion of the distillation, the residue is cooled to about 90° C. and about 360 parts of benzene are added. Cooling drops the temperature of the mixture to about 40° C. with precipitation of salt from the solution. The salt is removed by filtration and the removed salt carefully washed with about an additional 360 parts of benzene to remove polyether therefrom. The two benzene solutions are combined and distilled to separate the benzene. When the kettle temperature reaches 125° C. vacuum is applied and distillation continued to a kettle temperature of 170° C. at 25 millimetres pressure. The resulting liquid glycidyl polyether of 2,2-bis(4-hydroxyphenyl)propane has the following properties:—

	Durrans' melting point	- - -	9° C.
	Molecular weight	- - -	370
	Epoxide value (epoxide equivalents per 100 grams)	- - -	0.50
25	Epoxide equivalent weight	- - -	200
	Hydroxyl value (hydroxyl equivalents per 100 grams)	- - -	0.08
	Per cent. chlorine	- - -	0.46
30	From the above values, n is 0.106 so the average molecular of the polyether contains 1.106 of the aromatic radicals therein. The 1,2-epoxy equivalency of the product is 1.85.		

POLYETHER L—2

35 A solution consisting of 11.7 parts of water, 1.22 parts of sodium hydroxide, and 13.38 parts of 2,2-bis(4-hydroxyphenyl)propane is prepared by heating the mixture of ingredients to 70° C. and then cooling to 46° C. at which temperature 14.06 parts of epichlorhydrin are added while agitating the mixture. After 25 minutes have elapsed, there is added during an additional 15 minutes' time a solution consisting 5.62 parts of sodium hydroxide in 11.7 parts of water. This causes the temperature to rise to 63° C. Washing with water at 20° C. to 30° C. temperature is started 30 minutes later and continued for 4½ hours. The product is dried by heating to a final temperature of 140° C. in 80 minutes, and cooled rapidly. At room temperature, the product is an extremely viscous, semi-solid having the following properties:—

55	Durrans' melting point	- - -	23° C.
	Molecular weight	- - -	460
	Epoxide value (equivalents epoxide per 100 grams)	- - -	0.409
	Epoxide equivalent weight	- - -	244
60	Hydroxyl value (equivalents hydroxyl per 100 grams)	- - -	0.20
	Per cent. chlorine	- - -	0.18
	The value of n is thus 0.42 and the 1,2-epoxy equivalency is 1.88.		

POLYETHER L—3

65 Resorcinol is dissolved in epichlorhydrin in the proportion of 1 mol of resorcinol to 10 of epichlorhydrin containing about 1% of water. Solid sodium hydroxide is added in three successive portions in a total amount of 2.04 mols per mol of resorcinol with a short heating up time, and rapid reaction and control of temperature. The product is isolated from benzene solution as described above with reference to Polyether L—1. The obtained glycidyl polyether of resorcinol is a viscous liquid having a Durrans' melting point of -9° C., an epoxide equivalent weight of 136.5 and a chlorine content of 0.40%.

POLYETHER L—4

80 A glycidyl polyether is prepared from 142 parts of 1,1-bis(4-hydroxyphenyl)ethane dissolved in 644 parts of epichlorhydrin. The mixture is slowly heated to 70° to 80° C. and a total of 54.5 parts of solid caustic pellets are slowly added. The temperature rises to about 115° C., but falls to 100° C. as water forms during the reaction, the reaction mixture being refluxed. After about 1.5 hours' reaction time, the excess epichlorhydrin is then distilled off under vacuum. 150 parts of benzene is added to the residue and the mixture is filtered free of salt. The filtered salt is washed with a like amount of fresh benzene and the washing combined with the benzene solution of product. The benzene and traces of epichlorhydrin are then removed from the product by vacuum distillation at pressure of 0.5 millimetres (mercury) up to a temperature of about 165° C. The resulting liquid glycidyl polyether has the following properties:—

	Durrans' melting point	- - -	2° C.
	Molecular weight	- - -	342
	Epoxide value (equivalents epoxide per 100 grams)	- - -	0.540
	Epoxide equivalent weight	- - -	185
	Hydroxyl value (equivalents hydroxyl per 100 grams)	- - -	0.08
	Per cent. chlorine	- - -	0.73
	Calculation gives $n=0.06$ and the 1,2-epoxy equivalency is 1.85.		

POLYETHER L—5

115 A solution of 100 parts of 1,1-bis(4-hydroxyphenyl)-2-ethylhexane dissolved in 308 parts epichlorhydrin containing 1.3 parts of water is heated to 90° C. Then 27.7 parts of sodium hydroxide are added at a rate sufficient to keep the reaction mixture refluxing at 95° to 100° C. from the heat of reaction. The excess epichlorhydrin is stripped out to a final temperature of 150° C. under 10 millimetres pressure of mercury. Two hundred parts of benzene are added, the precipitated sodium chloride removed by filtration and benzene distilled off to a final temperature of 180° C. at 8 to 10 millimetres (mercury) pressure. The resulting viscous glycidyl polyether has the following properties:—

- Durrans' melting point - - - 14° C.
 Molecular weight - - - 441
 Epoxide value (equivalents
 epoxide per 100 grams) - - 0.39
 Epoxide equivalent weight - 256
 Hydroxyl value (equivalents
 hydroxyl per 100 grams) - 0.12
 Per cent. chlorine - - - 1.3
 With this product, $n=0.18$ and the 1,2-
 epoxy equivalency is 1.72. Preparation and prop-
 erties of high melting glycidyl polyethers will
 next be exemplified.

POLYETHER H—1

- In a vessel fitted with an agitator, 228 parts
 of 2,2-bis(4 hydroxyphenyl)propane and 55
 parts of sodium hydroxide as a 10% aqueous
 solution are introduced and heated to about
 45° C. whereupon 113 parts of epichlorhydrin
 are added rapidly while agitating the mixture
 The temperature of the mixture is then gradu-
 ally increased and maintained at about 95° C.
 for 80 minutes. The mixture separates into a
 two-phase system and the aqueous layer is
 drawn off from the product of syrupy consis-
 tency which forms. The latter is washed with
 hot water while molten until the wash water
 is neutral to litmus. The product is then
 drained and dried by heating to a final tem-
 perature of 130° C. The resulting solid gly-
 cidyl polyether has the following properties:—
 Durrans' melting point - - - 98° C.
 Molecular weight - - - 1400
 Epoxide value (equivalents
 epoxide per 100 grams) - - 0.12
 Epoxide equivalent weight - 834
 Hydroxyl value (equivalents
 hydroxyl per 100 grams) - 0.348
 Per cent. chlorine - - - 0.14
 The value of n is 3.74 and the 1,2-epoxy
 equivalency is 1.68.

POLYETHER H—2

- To 100 parts of Polyether L—1, there are
 added 45 parts of 2,2-bis(4-hydroxyphenyl)
 propane and the mixture is heated at 200° C.
 for 90 minutes with occasional stirring. The
 proportion of dihydric phenol is such that
 about 0.78 equivalent of phenolic hydroxyl
 group is initially present per equivalent of
 epoxide in the glycidyl polyether. The resulting
 solid product has the following properties:—
 Durrans' melting point - - - 86° C.
 Molecular weight - - - 1230
 Epoxide value (equivalents
 epoxide per 100 grams) - - 0.117
 Epoxide equivalent weight - 855
 Hydroxyl value (equivalents
 hydroxyl per 100 grams) - 0.354
 Per cent. chlorine - - - 0.32
 This high melting thermoplastic glycidyl
 polyether of 2,2-bis(4-hydroxyphenyl)propane
 has $n=3.1$ and a 1,2-epoxy equivalency of
 1.44.

POLYETHER H—3

- To 100 parts of Polyether H—1 heated to
 about 150° C. there are added 5 parts of 2,2-

bis(4 hydroxyphenyl)propane. The heating is
 continued for about 2 hours while stirring and
 gradually increasing the temperature to 200°
 C. The resulting solid product has the follow-
 ing properties:—

- Durrans' melting point - - - 122° C.
 Molecular weight - - - 2900
 Epoxide value (equivalents
 epoxide per 100 grams) - - 0.06
 Epoxide equivalent weight - 1670
 Hydroxyl value (equivalents
 hydroxyl per 100 grams) - 0.37
 Per cent. chlorine - - - 0.13

The value of n is 9.0 and the 1,2 epoxy
 equivalency is 1.7.

POLYETHER H—4

By using 7.75 parts of 2,2-bis(4 hydroxy-
 phenyl)propane with 100 parts of Polyether
 H—1 and effecting the reaction under the same
 conditions as described above for Polyether H—3,
 there is obtained glycidyl polyether hav-
 ing the following properties:—

- Durrans' melting point - - - 148° C.
 Molecular weight - - - 3750
 Epoxide value (equivalents
 epoxide per 100 grams) - - 0.036
 Epoxide equivalent weight - 2780
 Hydroxyl value (equivalents
 hydroxyl per 100 grams) - 0.40
 Per cent. chlorine - - - 0.13

This solid product has $n=12.0$ and an
 epoxide equivalency of 1.35.

The compositions of the present inventions
 are prepared from the above-described poly-
 ethers by adding and mixing 3 to 20 parts,
 preferably 5 or 10 parts, by weight of small
 particles of any one of Polyether H—1, H—2,
 H—3 or H—4 with 100 parts by weight of
 any one of Polyether L—1, L—2, L—3, L—4
 or L—5 heated to about 80° C. to 100° C.,
 and continuing the heating at such temperature
 until the particles dissolve and homogenise,
 which occurs in not over about 2 hours' time.
 Upon cooling to room temperature of about
 25° C. the compositions are liquid although
 some have high viscosity.

Viscosity data on certain compositions of the
 present invention are tabulated below, the vis-
 cosity having been measured with a Brookfield
 Viscosimeter at 25° C. The viscosity of Poly-
 ether L—1 is 12,400 centipoises and that of
 Polyether L—2 is above 100,000 centipoises.
 The upper limits of measurement with the
 Brookfield Viscosimeter is 100,000 centipoises.
 The parts are by weight for the tabulated com-
 positions.

TABLE I.		
No.	Composition	Viscosity
	100 parts polyether L—1 plus:	
1	5 parts polyether H—1	30,200
2	5 parts polyether H—3	45,500
3	5 parts polyether H—4	54,600
4	10 parts polyether H—1	64,400
5	10 parts polyether H—3	89,300
6	10 parts polyether H—4	above 100,000

In order to effect cure, 4.76% by weight of piperidine was added to each of Compositions Nos. 1 to 3, and 4.55% by weight to each of Compositions Nos. 4 to 6. The mixtures were then heated for 24 hours in an air oven set at 60° C. The resulting cured resins were hard and tough.

Various optional ingredients can be incorporated with the compositions of the present invention. Their choice and amount is largely governed by the particular use to which the compositions are put.

Certain compositions of the present invention may contain a cyano-substituted hydrocarbon as viscosity reducing diluent. They are normally liquid in having a melting point below 10° C. and contain one or more nitrile groups linked to the hydrocarbon radical which may be of any type desired, saturated or unsaturated; aliphatic, alicyclic or aromatic. Although it has been found that acetonitrile or methyl cyanide is particularly preferred, examples of other suitable compounds include propionitrile, butyronitrile, capronitrile, laurionitrile, acrylonitrile, methacrylonitrile, crotonitrile, oleonitrile, 2-cyano-1,3-butadiene, succinonitrile, glutaronitrile, adiponitrile, fumaronitrile, allylmalononitrile, cyclopentyl cyanide, cyclohexyl cyanide, 1,2-dicyanocyclohexane, benzonitrile, and phenyl-acetonitrile. In general, it is preferred to employ a cyano-substituted saturated hydrocarbon containing one to two cyanide groups, which compound contains 2 to 8 carbon atoms. Good results are obtained with alkyl cyanides containing up to 4 carbon atoms, although higher members of this class containing up to 12 carbon atoms and having melting points below 10° C may be used, if desired.

The compositions may also contain one or more comminuted inorganic fillers such as asbestos, aluminium oxide, silica, bauxite, zinc oxide, china clay, titanium oxide and silicon carbide.

In using the composition for adhesive purposes in metal-to-metal bonding, it has been found useful also to include an inert solid comminuted filler in the composition in amount of about an added 5% to 400% by weight based upon the low melting glycidyl polyether in the composition. Inorganic fillers such as iron oxide or asbestos, not only contribute to the shear strength of the cured resin bond, but also improve the retention of high strength at elevated temperatures.

In using the compositions of the present invention, a hardening agent is incorporated therewith. Upon the addition of the hardening agent, the composition begins to cure and harden even at ordinary temperature. A great variety of substances are now known to be hardening agents for the resin-forming ingredients of the composition such as alkalis like sodium or potassium hydroxide; alkali phenoxides like sodium phenoxides; carboxylic acids or anhydrides such as formic acid, oxalic

acid or phthalic anhydride; Friedel-Crafts metal halides like aluminium chloride, zinc chloride, ferric chloride, or boron trifluoride, as well as complexes thereof with ethers, acid anhydrides, ketones and diazonium salts; phosphoric acid and partial esters thereof including *n*-butyl orthophosphate, diethyl orthophosphate and hexaethyl tetraphosphate; and amino compounds such as triethyl amine, ethylene diamine, diethyl amine, diethylene triamine, triethylene tetramine, pyridine, piperidine, *N,N*-diethyl-1,3-propanediamine, dicyandiamide and melamine. The hardening agent is added and mixed in with the composition in order to effect hardening. The amounts vary considerably depending upon the particular agent employed. For the alkalis or phenoxides, 2 to 4 per cent is suitable. With phosphoric acid and esters thereof, good results are obtained with 1 to 10 per cent added. The amino compounds are used in amounts of about 5 to 15 per cent and the others involve the addition of about 1 to 20 per cent.

When using the composition of the present invention for adhesive purposes, the composition, which may also contain various optional constituents, has added thereto sufficient hardening agent and the mixture is applied as by spreading upon a surface desired to be united to another surface as a layer of about 0.0005 to 0.1 inch thickness. The adhesive mixture is suitable for uniting various surfaces such as wood to wood, wood to metal, metal to metal, resin to resin, or any combination thereof. After application and joinder of the surfaces desired to be united, the adhered articles are allowed to cure for a period of from about 30 minutes to a day or more, depending upon the hardening agent and temperature employed. In this time when heating is omitted, the adhesive composition will set up to a solid which will permit ordinary handling thereof. Maximum strength for the adhesive layer will be reached within one day to two weeks. While the application is effected at ordinary atmospheric temperature and the curing may also be permitted to occur at such temperature, the curing may be effected in shorter times at elevated temperatures such as up to 75° C., 100° C., 150° C., or even higher in some cases. In cases where elevated curing temperature is employed, the chosen temperature is below the boiling temperature of the lowest boiling constituent contained in the mixture, and preferably, it is at least 20° C. below such boiling temperature.

The cured resin from the compositions of the present invention has very high physical strength and toughness as may be observed by subjecting the resin to thermal shock tests. Like other resinous materials, the cured resin has low heat conductivity. If a sizable sample of the resin is thrust into a medium of appreciably different temperature from the initial temperature of the sample, great physical strain occurs in the outer part of the sample from

thermal expansion or contraction with the result that the sample will crack unless it has the strength and toughness needed to withstand the test. For example, a 50 gram sample of the composition containing 100 parts by weight of Polyether L—1 and 10 parts of Polyether H—3 was prepared and placed in a paper cup along with another 50 gram sample of Polyether L—1 alone in another cup. To each were added 2.5 grams of piperidine as curing agent. The samples were resinsified to hard resins by heating for 24 hours in an oven set at 60° C. The paper cups were removed and the cured resin samples were subjected to the following thermal shock test. The samples were placed in an oven set at 150° C. for ½ hour, then removed and allowed to cool at room temperature for ½ hour, next thrust into crushed solid carbon dioxide (dry ice) at about -70° C. for ½ hour, and then allowed to warm at room temperature during ½ hour. This cycle was then repeated. It was found that the resin sample from resinsification of Polyether L—1 alone cracked in the hot portion of the fifth cycle. On the other hand, the resin sample from the composition of the invention passed seven cycles without cracking and then also passed fifty more cycles as described except that the oven temperature was increased to 200° C. The test was then stopped without this resin sample being fractured or cracked.

When employed in adhesive formulations, the compositions of the invention have the important advantage of imparting to the cured resin bond great resistance against mechanical shock. In other words, the impact strength obtained with cured adhesives from the compositions containing the mixture of high melting and low melting glycidyl polyethers is markedly higher than that obtained with a

cured adhesive from a single glycidyl polyether. The impact strength or resistance against mechanical shock is of prime importance especially when the adhesives are employed for metal to metal bonding.

The compositions of the present invention when employed in adhesive formulations have a high shear strength both at low and at high temperatures. Therefore the compositions can be utilized in many applications for which prior compositions were unsuitable because they did not retain high shear strength at elevated temperatures.

The unusually high impact strengths obtained with compositions of the invention will be illustrated. Formulations were prepared containing the constituents and amounts given in Table II below. Allyl glycidyl ether was incorporated in the formulations in such amounts as to render the compositions liquid. A formulation employing a single glycidyl polyether was included for comparison. The parts were by weight. To each composition there were added 8 parts of N,N-diethyl-1,3-propanediamine as curing agent. The freshly prepared mixtures were spread on a one-inch square surface of clean aluminium blocks of about one-quarter inch thickness with a 5 millimetres doctor blade. Coated surfaces of two blocks were joined and the adhesive cured by heating the joined blocks in an oven for 45 minutes at 200° F. After cooling the Izod impact strength was determined according to ASTM method D-950-471. The results are given in the following table. For the compositions of the present invention, it was found that the impact strength was greater than the limit of the testing machine and amounted to more than 15 foot-pounds per square inch.

	Low Melting Polyether	High Melting Polyether	Allyl Glycidyl Ether as Diluent	Impact Strength foot-pounds per square inch
	100 parts L—1	10 parts H—1	1 part	>15.0
	100 parts L—1	10 parts H—2	3.5 parts	>15.0
	100 parts L—1	10 parts H—3	4.5 parts	>15.0
	85 parts L—2	none	15 parts	1.6

The compositions of the present invention are very useful in adhesives for joining a variety of metals as will be evident from the following. The composition consisted of 100 parts by weight of Polyether L—1 containing 5 parts of Polyether H—3 to which were added 5 parts of piperidine as curing agent. The freshly prepared mixture was spread on a one-inch square surface of each of two blocks of the metals listed in Table III below with a 5 millimetres doctor blade. The coated surfaces were joined

and the adhesive was cured by baking the joined blocks in an oven for 24 hours at 60° C. After cooling, the blocks were subjected to the 100 block shear test of the United States Army-Navy-Civil Committee on Aircraft Design Criteria: "Wood Aircraft Inspection and Fabrication", ANC—19 (Dec. 20, 1943), discussed in an article by R. C. Rinker and G. M. Kline, Modern Plastics, Volume 23, page 164, 1945. The shear strengths at 77° F. for the blocks were as follows:—

TABLE III.

	Block Material	Shear Strength Pounds per square inch
5	Aluminium (24ST)	3030
	Aluminium (Alclad)	5390
	Magnesium	2045
	Stainless steel (18—8)	4045
	Copper	3670
10	Brass	1965
	Hot rolled steel	2740
	Cold rolled steel	3120
	Cold plated steel	1460
	Silver plated steel	1770
15	Nickel	4975

Certain preferred compositions of the present invention containing an aliphatic polyepoxide and their performance will be illustrated in the following examples. The parts are by weight.

20 In testing the compositions, the freshly prepared adhesive mixture of the composition and the curing agent was applied to clean aluminium sheets with a 5 millimetres doctor blade, the coated surfaces were joined, and after

25 baking to effect cure, the tensile shear strength

and the bend strength were determined as described in U.S.A.F. Specification 14164. The impact strength was determined according to ASTM method D—950—47T with clean aluminium blocks prepared in like manner. 30

EXAMPLE 1.

Base compositions were prepared containing 100 parts of Polyether L—1, 10 parts of Polyether H—4, and 12 parts of epoxidised soybean oil. The epoxidised soybean oil contained about 3.6 epoxy groups per molecule and was the same as the epoxidised oil to be referred to in subsequent examples. Fine asbestos fibre (Johns-Manville 7TF—2) in amounts listed in the following table along with 10 parts of N,N-diethyl-1,3-propanediamine were added to and mixed with the base compositions. The freshly prepared adhesive mixture was tested for joining aluminium, cure being effected by baking for 45 minutes at 200° F. in an oven. In all cases, the impact strength at both —70° F. and 180° F. was found to be more than 15 foot-pounds per square inch. The tensile shear strength in pounds per square inch (psi) and the bend test results are tabulated below:—

	Parts of Asbestos	Tensile Shear Strength, psi at 77° F.	at 180° F.	Bend Test, lbs. at 77° F.
55	0	2585	1960	144
	20	3115	2880	200
	30	3600	3560	180
	40	3220	3090	176
	50	3390	2810	184

It will be observed from the foregoing results that the composition of the present invention in cured condition gives very high shear strengths not only at room temperature (77° F.) but also at the elevated temperature of test, 180° F.

65 EXAMPLE 2.

The effect of various amounts of epoxidised soybean oil in the composition will be illus-

trated in this example. Each mixture contained 100 parts of Polyether L—1, 10 parts of Polyether H—4, 30 parts of the fine asbestos fibre and 8 parts of N,N-diethyl-1,3-propanediamine as well as the amounts of the epoxidised soybean oil listed in the table below. The mixtures were applied as adhesive to aluminium and cured by baking for 45 minutes at 200° F. 75

	Parts of Epoxidised Soybean Oil	Tensile Shear Strength, psi at 77° F.	at —70° F.
80	8	2790	2300
	10	3500	2565
	12	3250	2725
	16	3285	2515
	20	3245	2370

It will be noted from the foregoing results that very high shear strengths at the low temperature of —70° F. are obtained.

EXAMPLE 3.

The use of other liquid aliphatic poly-

epoxides in the composition will be illustrated in this example. Base mixtures were prepared containing 100 parts of Polyether L—1, 10 parts of Polyether H—4, and 30 parts of the fine asbestos fibre. The adhesive mixtures also contained the liquid aliphatic polyepoxides

given in the table below in the amounts indicated and the listed amounts of N,N diethyl-1,3-propanediamine as curing agent. The mix-
tures were applied as adhesives to aluminum and cured by baking for 45 minutes at 200° F. The results follow:

10	Liquid Polyeпоxide	Parts Curing Agent	Tensile Shear Strength, psi, at:			
			70° F.	77° F.	180° F.	77° F. after 1 hour in boiling H ₂ O
10	12 parts epoxidised soybean oil	8	2620	3390	3445	3400
	4 parts diglycidyl monoether	8	2185	2510	—	—
	8 " " " "	8	2025	3100	—	2760
	12 " " " "	8	2000	2890	2850	2560
15	16 " " " "	8	1980	2670	—	2540
	8 " polyallyl glycidyl polyether	10	2730	3130	2825	—
	12 " " " "	12	2735	2970	2810	—
	16 " " " "	16	3090	3500	3265	—

EXAMPLE 4.

20 The preferred composition of the present invention contains 100 parts of Polyether L—1, 10 parts of Polyether H—4, 12 parts of the employed in adhesive use of the composition asbestos fibre. Various curing agents were
25 employed in adhesive use of the composition for joining aluminium, the cure being effected by baking for 45 minutes at 200° F. The

results are given in the following table which indicates the amount of curing agent used in the composition. For brevity, the curing agents identified as "Triacetate", "Triisobutyrate", etc., were amine salts prepared by neutralising one mol of 2,4,6-tri(dimethylaminomethyl) phenol with three mols of the appropriate fatty acid to form the indicated salt. 35

40	Curing Agent Parts and Name	Tensile Shear Strength, psi			Bend Test,
		70° F.	77° F.	180° F.	lbs. at 77° F.
40	5 dimethylethanolamine	2830	3505	3600	189
	8 dimethylethanolamine acetate	2820	3630	3405	197
	10 triacetate	2430	3320	3180	166
	12 triisobutyrate	2485	3535	2785	—
	16 tricaproate	2235	3210	1810	174
	17.5 trilaurate	2490	3355	1605	158
45	19.3 trimyristate	2535	3500	1655	177

EXAMPLE 5.

50 The use of various finely divided fillers in a preferred composition of the present invention will be illustrated. In each case, the base composition consisted of 100 parts of Polyether L—1, 10 parts of Polyether H—4 and 12 parts of the epoxidised soybean oil as well as the amount and kind of filler listed in the table

below and 10 parts of N,N-diethyl-1,3-propanediamine as curing agent. Before adding the curing agent, all the compositions except the first had approximately the same viscosity. The mixtures were tested as adhesives for aluminium, cure being effected by baking for 3 hours at 200° F. The results follow:— 60

	Filler	Parts Filler	Tensile Shear Strength, psi	
			at 77° F.	at 180° F.
5	None - - - -	0	2715	1355
	Asbestos - - - -	30	3330	2795
	Zinc oxide - - - -	122	2395	2660
	Titanium oxide - - - -	163	2465	3080
	Calcium oxide - - - -	106	2835	2680
10	Nickelic oxide - - - -	244	2370	3050
	Lead oxide - - - -	264	2475	3415
	Manganese oxide - - - -	346	2610	2805
	Cupric oxide - - - -	382	2535	1920
	Stannic oxide - - - -	130	2507	2815
15	Ferric oxide - - - -	122	2795	3480
	Alumina - - - -	85	2835	3250
	Glass floc - - - -	38	3185	1840
	Hydrated silicon dioxide - - - -	20	3485	3075
	Cellulose floc - - - -	8	2515	1820
20	Silica - - - -	8	2245	1825
	Nylon floc - - - -	25	3285	2005
	Rice hull floc - - - -	61	2885	2015

EXAMPLE 6.

The use of various times and temperatures of cure will be illustrated. There was employed the preferred composition containing 100 parts of Polyether L—1, 10 parts of Polyether H—4, 12 parts of the epoxidised soybean oil, and 30

parts of fine asbestos fibre to which was added 8 parts of N,N-diethyl-1,3-propanediamine. The mixtures were again employed as adhesives to bond aluminium together using the times and temperatures of cure indicated in the following table:—

Cure Conditions	Tensile Shear Strength, psi		
	at -70° F.	at 77° F.	at 180° F.
2 hrs. at 165° F. - - - -	2115	3215	3640
45 min. at 200° F. - - - -	2620	3390	3445
45 min. at 240° F. - - - -	3180	3270	2860

EXAMPLE 7.

For purposes of comparison, the performance of a composition of the present invention will be contrasted with the performance of a similar composition which contained furfural, a viscosity reducing diluent recommended by prior workers in the art, in place of a liquid aliphatic polyepoxide. The composition of the present invention contained 100 parts of Polyether L—1, 10 parts of Polyether H—4, 12 parts of the epoxidised soybean oil and 30 parts of the

fine asbestos fibre to which were added 10 parts of N,N-diethyl-1,3-propanediamine as curing agent to form an adhesive mixture. The other adhesive mixture contained the same kind and amounts of constituents except that 12 parts of furfural were substituted for the 12 parts of epoxidised soybean oil. The two mixtures were tested as adhesives to join aluminium, cure being effected by baking for 45 minutes at 200° F. The results follow:—

Viscosity Reducing Component.	Tensile Shear Strength, psi		
	at -70° F.	at 77° F.	at 180° F.
Furfural - - - -	2555	2725	1525
Epoxidised soybean oil - - - -	2800	3570	3630

It will be observed that the shear strengths obtained with the composition of the present invention are much superior to those obtained with the corresponding composition containing furfural. This is especially true for the strengths at the elevated temperature of 180° F. where composition of the invention gives a strength

almost 250% greater than that from the furfural-containing composition.

What we claim is:—

1. A composition of matter comprising a first glycidyl polyether of a dihydric phenol in admixture with an added 3% to 20% by weight of a second glycidyl polyether of a di-

5 hydric phenol, said first glycidyl polyether having a Durrans' Mercury Method melting point below 80° C., a 1,2 epoxy equivalency as
 10 hereinafter defined between 1.6 and 2.0, and containing 1 to 1.5 of the aromatic radicals in the average molecule thereof; and said second glycidyl polyether having a Durrans' Mercury Method melting point above 75° C., a 1,2-
 15 epoxy equivalency as hereinafter defined of 1.2 to 1.8 and containing at least 4 of the aromatic radicals in the average molecule thereof.

2. A composition as claimed in claim 1, comprising also a liquid aliphatic polycarbonate as hereinafter defined having a viscosity of less
 20 than 500 centipoises at 25° C.

3. A composition as claimed in claim 1 or claim 2, wherein the dihydric phenol of both glycidyl polyethers is 2,2-bis(4-hydroxyphenyl) propane, and the Durrans' Mercury Method
 25 melting point of the first glycidyl polyether is below 15° C. and that of the second is between 125° C. and 180° C.

4. A composition as claimed in any one of the preceding claims, wherein the percentage by weight of the second glycidyl polyether is 5 to 10%, the dihydric phenol of both glycidyl polyethers is 2,2-bis(4-hydroxyphenyl)propane, and the Durrans' Mercury Method melting
 30 point of the first glycidyl polyether is from 5° C. to 12° C. and that of the second glycidyl

polyether is from 140° C. to 160° C.

5. A composition as claimed in any one of claims 2 to 4, wherein the liquid aliphatic polycarbonate is an epoxidised triglyceride, containing 2.5 to 5 epoxy groups per molecule. 35

6. A composition as claimed in any one of claims 2 to 4, wherein the liquid aliphatic polycarbonate is diglycidyl monoether or polyallyl glycidyl ether. 40

7. A process for the preparation of a composition of matter substantially as hereinafter described with reference to the specific examples.

8. A composition of matter substantially as hereinafter described with reference to the specific examples. 45

9. A resin prepared by curing a composition of matter as claimed in any one of the preceding claims 1 to 6 and 8. 50

10. A composition suitable for use as an adhesive and comprising a composition of matter as claimed in any one of claims 1 to 6 and 8 and a curing agent.

11. A method of adhesively uniting surfaces which comprises introducing between the surfaces a composition as claimed in claim 10 and allowing or causing curing to take place. 55

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